Photoelectrochemical Hydrogen Production

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Objectives

- Develop low-cost, thin-film metal-oxide materials with suitable properties for use in "Hybrid Photoelectrodes" (*HPE*) for solar water splitting.
- Develop optimized *HPE* designs based on best available thin-film metal-oxide and photovoltaic-grade semiconductor materials.
- Demonstrate stable water splitting using *HPEs* based on best available materials systems.
- Demonstrate 7.5% solar-to-hydrogen (STH) efficiency with 1000 hour life by 2005; demonstrate 9% STH with 2000 hour life by 2010.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Material Durability
- N. Materials and System Engineering
- O. Photoelectrochemical Efficiency

Specific technical issues for durability and efficiency in the UH hybrid designs include the development of 'low-temperature' (<300°C) processes which yield photoactive and stable metal-oxide films compatible with hybrid photoelectrode fabrication, and continued development of optimized materials and device designs are needed to meet program goals.

Approach

Materials Research: Current focus on developing low-temperature reactive sputtering process to produce photoactive and stable metal-oxide films including Fe_2O_3 and WO_3

- *Partnership Support (Duquesne University & others):* to develop further understanding of structure and composition of photoactive metal oxides for the engineering of new, process-compatible materials.

Photoelectrode Testing: Current focus on incorporating best available materials into **"**Hybrid Photoelectrode" structures to evaluate performance and stability

- *Partnership Support (University of Toledo):* to design and fabricate multi-junction amorphous-silicon alloy devices with specified voltage and current characteristics.

Photoelectrode Optimization: Continued development of optimized materials and device designs for use in high-performance / low-cost **"**Hybrid Photoelectrodes ."

Accomplishments

Fe_2O_3 films successfully deposited using low-temperature sputter process:
- Ability to engineer key film properties successfully demonstrated.
- Excellent film adhesion and stability in alkaline media achieved.
- Photocurrents up to 0.1 mA/cm^2 achieved under 1-sun (typical outdoor sunlight without concentration) in films deposited to date.

WO_3 films successfully deposited using low-temperature sputter process:
- Ability to engineer key film properties successfully demonstrated.
- Excellent film adhesion and stability in acid media achieved.
- Photocurrents up to 1.2 mA/cm^2 achieved under 1-sun in films deposited to date.

Stable operation of "Hybrid Photoelectrode" demonstrated:
- Structure: amorphous silicon alloy tandem (University of Toledo) with sputtered indium tin oxide (ITO) and low-temperature sputtered WO_3 (UH) - 2.5 cm^2 area.
- Stable hydrogen production in 1 N H_2SO_4 measured for over 10 hours.
- Photocurrents up to 0.5 mA/cm^2 in 1-sun outdoor tests (0.7% STH).
- Performance consistent with measured properties of the WO_3 material and the tandem silicon cell.
- Analysis indicates significant efficiency enhancement possible with improved metal-oxide properties.

Future Directions

- Continued development of the "Hybrid Photoelectrode" using in-house and partnership resources.
- Expand efforts to optimize hybrid-compatible materials for efficiency and long-life.
- Design, fabricate and test "Hybrid Photoelectrodes" incorporating optimized materials.

Introduction

Under the sponsorship of the U.S. Department of Energy (DOE), the Thin Films Laboratory at the Hawaii Natural Energy Institute of the University of Hawaii (UH) has been developing high-efficiency, potentially low-cost, photoelectrochemical (PEC) systems to produce hydrogen directly from water using sunlight as the energy source. The main thrust of the PEC systems research at UH has been the development of integrated multi-junction photoelectrodes based on low-cost semiconductor, catalytic, and protective thin films [1].

Figure 1 shows a generic planar photoelectrode structure, where sunlight absorbed in photoactive regions produces electricity to drive the hydrogen evolution reaction (HER) and the oxygen evolution reaction at opposite surfaces. In order to meet the DOE's goals, the photoelectrode system must be

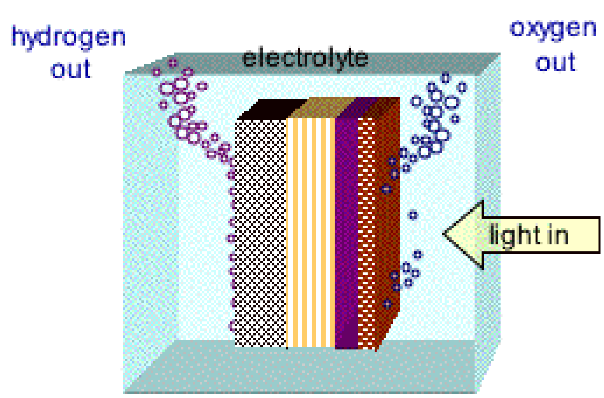

Figure 1. Generic Planar Photoelectrode Structure With Hydrogen and Oxygen Evolved at Opposite Surfaces

low-cost, and it must be capable of operating stably in corrosive aqueous electrolyte environments with solar-to-hydrogen (STH) conversion efficiencies greater than 7.5% by 2005, 9% by 2010 and greater than 10% by 2015 [2]. In an attempt to meet the cost and performance goals, UH has been concentrating on the development of a "Hybrid Photoelectrode" (*HPE*) which incorporates low-cost metal-oxide and photovoltaic-grade semiconductor thin films, as described in the following section.

Approach

The basic "Hybrid Photoelectrode" structure developed at UH is shown in Figure 2. This multi-junction device combines thin-film solid-state with PEC junctions to meet the voltage, current and stability requirements for hydrogen production. The design approach has relied on continued use of integrated models for photoelectrode design [3], establishment of industry and university partners with thin-film materials expertise, and fabrication and evaluation of photoelectrode test devices. Significant advantages of the *HPE* design over other structures investigated at UH [4] include elimination of lateral current collection; simplification of device geometry for ease of fabrication; and improved stability based on the thick, seamless outer metal-oxide layer.

The primary focus of our current work has been the development of *HPE*s based on low-cost solid-state junction materials such as amorphous silicon (a-Si) and copper-indium-gallium-diselenide (CIGS) coated with photoactive nano-structured metal oxides such as iron oxide (Fe_2O_3) and tungsten trioxide (WO_3). There has been extensive investigation into these metal-oxide films for their PEC water splitting properties; Figure 3, for example, shows hydrogen-production characteristics for Fe_2O_3 films deposited by spray-pyrolysis at Duquesne University [5] and for pyrolytic WO_3 films developed at the University of Geneva [6]. It can be seen that hydrogen currents can be quite high in the metal-oxide PEC junctions, but only at sufficient levels of voltage bias. In the *HPE* configuration, the necessary voltage bias is automatically generated in the buried solid-state junction utilizing low-energy photons not absorbed at the PEC interface.

Unfortunately, fabrication of hybrids using pyrolytic oxides is not possible at this time, since substrate temperatures for the established pyrolysis

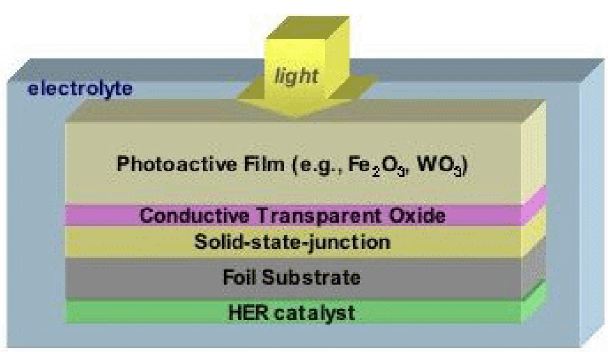

Figure 2. The Multi-Junction "Hybrid Photoelectrode" Structure, Showing Constituent Thin-Film Layers (Photons are absorbed both at the metal-oxide/electrolyte interface and at the buried solid-state junction.)

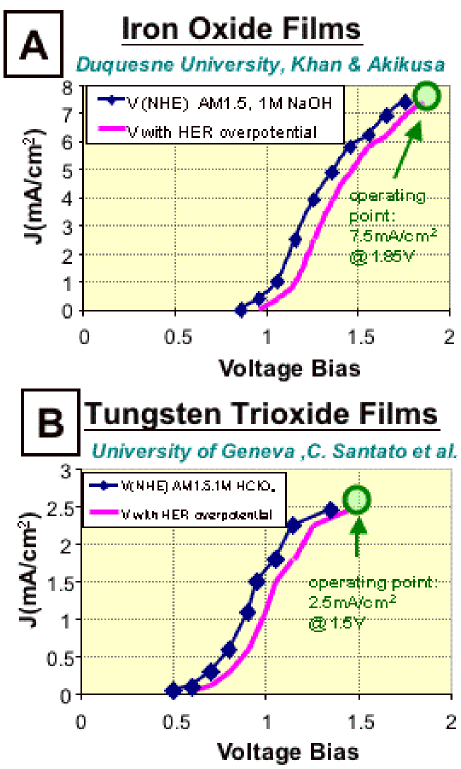

Figure 3. Published Photoelectrochemical Hydrogen Production Characteristics of Metal-Oxide Thin Films: A. Fe_2O_3 film (Duquesne University); B. WO_3 film (University of Geneva)

processes, generally exceeding 400°C, are high enough to damage the underlying solid-state junction. It has therefore been an important part of our research approach to develop low-temperature (<300°C) processes yielding photoactive and stable metal-oxide films. Specific emphasis has been on developing low-temperature reactive-sputter processes for Fe_2O_3 and WO_3 films, along with fabrication and testing of *HPE* prototypes using amorphous silicon solid-state junctions (fabricated at the University of Toledo) with the best available sputter-deposited oxide films.

Results

Significant progress was made this year in the development of low-temperature reactively-sputtered metal-oxide films for use in water-splitting “Hybrid Photoelectrodes”, and in the demonstration of operational devices using these materials. Importantly, all project milestones in materials research and photoelectrode development have been met to date.

A key milestone in our materials research was the successful fabrication of photoactive Fe_2O_3 and WO_3 films using low-temperature reactive sputtering processes. Reactive sputtering is a vacuum deposition technique [7] where a range of process parameters, including substrate temperature, ambient gas partial pressures, and sputtering power, can influence film characteristics. We found, for example, that structural, electronic and photoelectrochemical properties of sputtered Fe_2O_3 and WO_3 films could be significantly altered by varying oxygen partial pressure and substrate temperature.

Figure 4 demonstrates the range of variations in grain structure (Figure 4a) and electronic conductivity (Figure 4b) observed in the sputtered iron-oxide films. It was found that the films deposited at the high end of our ‘low-temperature’ range (200°C) with low oxygen percentages (5%) exhibited the best conductivities (attributable to large grain structure and oxygen vacancy levels). Unfortunately, although they exhibited excellent stability in electrolyte, the hydrogen photocurrents in these films were limited to 0.1 mA/cm^2 in outdoor tests. In contrast, photocurrents up to 1.2 mA/cm^2 were readily achieved in the sputtered WO_3 films investigated to date, as seen in Figure 5a for a sample deposited at 200°C with 12% oxygen. Similar to the iron-oxide samples, the tungsten-trioxide films were stable in electrolyte, and also exhibited a process-dependent range of property variations. Figure 5b, for example, shows the WO_3 films’ conductivities, again with the highest observed in films deposited at 200°C with low oxygen percentages.

A critical milestone in our photoelectrode development effort was the successful demonstration of functional “Hybrid Photoelectrodes” using sputtered materials. The operational devices were fabricated using tandem amorphous silicon junctions (fabricated by the University of Toledo) coated with reactively-sputtered WO_3 films (1.0-2.0 µm). Ten photoelectrodes with an active area of 2.5 cm^2 have been fabricated to date and evaluated using the test structure shown in Figure 6a. All ten exhibited hydrogen photocurrent during outdoor testing, and importantly, the observed performances were consistent with analyses based on behavior of the silicon and tungsten-trioxide films used. Figure 6b

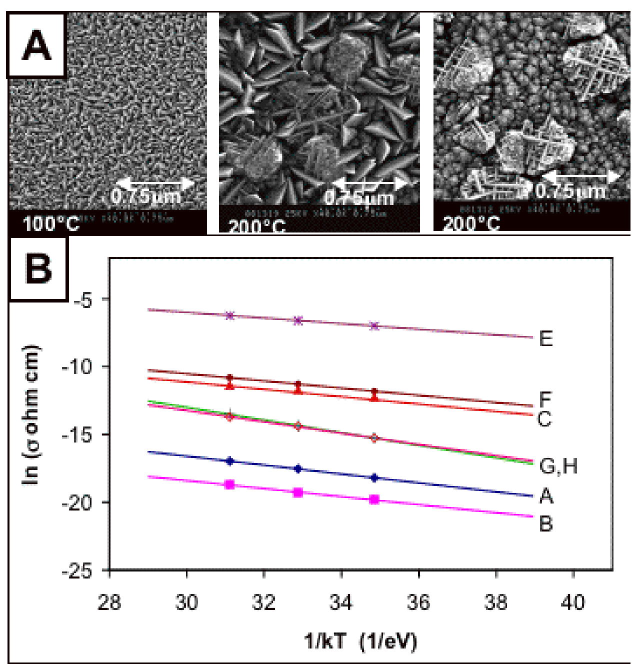

Figure 4. Measured Property Variations in Low-Temperature Sputtered Iron-Oxide Films: A) Grain Structure Dependence on Deposition Parameters; B) Large Variations in Electrical Conductivity

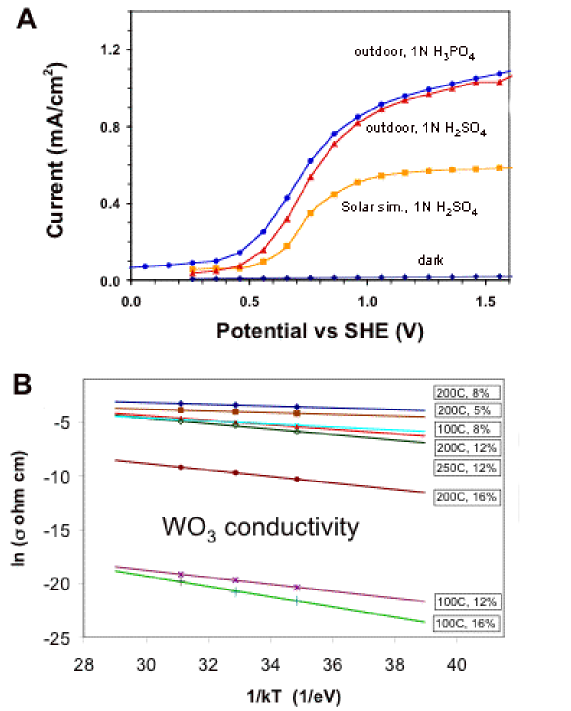

Figure 5. Properties of Low-Temperature Sputtered Tungsten-Trioxide Films: A) Photocurrents in Acid Media; B) Electrical Conductivity as a Function of Deposition Parameters

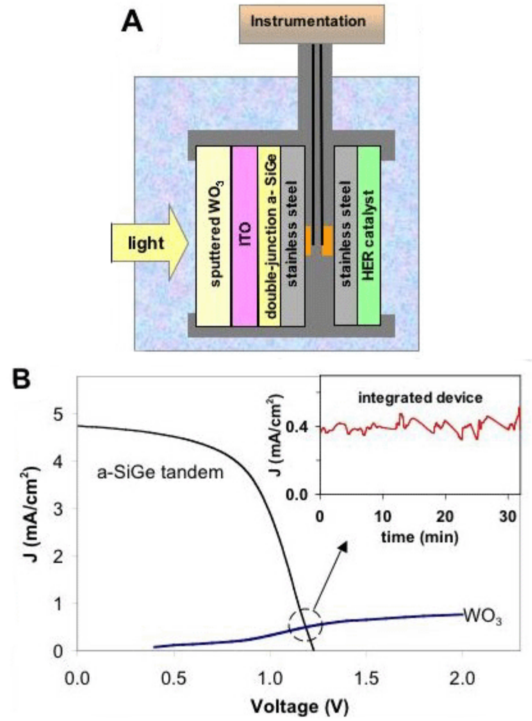

Figure 6. Successful "Hybrid Photoelectrode" Demonstration: A) Test Structure; B) Analysis Based on Performance of Component Films, and Measured Performance of the Integrated Device

shows the predicted 1-sun operating point of 0.45 mA/cm^2 for one of the test devices, consistent with the measured performance shown in the inset. The best devices tested to date have generated hydrogen at up to 0.8% STH without serious degradation over a 10-hour operating period. Although the efficiency is low in these initial prototypes, there is clear room for improvement by enhancing the WO_3 photocurrent levels, as seen in Figure 6b. On this basis, future plans must include heavy emphasis on the further materials development of metal-oxide films.

Conclusions

- The optical/electronic properties of present hybrid-compatible metal oxides have been identified as the *key limiting factor* to hydrogen-production efficiency in *HPE*s at this time, clearly defining the primary focus for continued research efforts.
- Expanded efforts to optimize hybrid-compatible materials for efficiency and life are needed.
- We are confident that with continued development and testing of *HPE*s based on best available materials from both in-house and partnership resources, we will be able to *meet the 2005 and 2010 program goals.*

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2. E. L. Miller, R. E. Rocheleau, S. Khan, "A Hybrid Multijunction Photoelectrode for Hydrogen Production Fabricated with Amorphous Silicon/Germanium and Iron Oxide Thin Films." International Materials Research Congress XI, Cancun, Mexico (2002).

Special Recognitions & Awards/Patents Issued

1. E. L. Miller & R.E. Rocheleau, "Hybrid Solid-State/Electrochemical Photoelectrode for Hydrogen Production": provisional patent with the UH *Office of Technology Transfer and Economic Development.*